USE OF BRIGHT PLATINUM ELECTRODES FOR MEASUREMENT OF ELECTROLYTIC RESISTANCES

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ABSTRACT. On account of certain difficulties with platinised electrodes, it is desirable to use bright electrodes in measurements of electrolytic resistances. It has been shown that the Wheatstone's bridge method gives as satisfactory results with bright electrodes as with platinised electrodes by using a two-electrode cell and

(1) an a. c. galvanometer of the wattmeter or of the dynamometer type through an amplifier,

(2) a low impressed voltage,

(3) a shunted capacitance in the R-arm and by making the ratio arms of equal resistance.

INTRODUCTION

After Kohlrausch introduced the use of alternating currents and electrodes coated with platinum black for the determination of electrolytic resistances, his method is almost invariably used for the purpose. The platinum black coating, although it effectively eliminates the disturbing effect of polarisation, has, however, certain inherent disadvantages, the notable among which are the following :—

(1) it adsorbs the solute molecules and so it is necessary to stir the solution from time to time (in order to keep the strength of the solution between the electrodes constant) and to clean the cell carefully when changing the solution ;

(2) it acts as a catalyst in the oxidation of certain substances, particularly dye-stuffs.

Attempts have, therefore, been made from time to time to avoid the coating altogether. Notable amongst the works in this line is that of Shedlovsky (1930), who recommended the use of multiple electrodes in the same cell. His final recommendation is, however, to platinise the electrodes slightly for the sake of consistency and constancy.

The present paper is an attempt in this direction using two-electrodes only.

DESIGN OF THE CELL

In designing the cell for strong electrolytes, the underlying idea is that the greater the ratio of the area of the electrodes to that of the cross-section of the current-carrying part of the solution, the less pronounced will be the effect of polarisation. For the solution of KCl, the form of the cell is that shown in Fig. 1. The area of each electrode is one sq., cm. whereas the

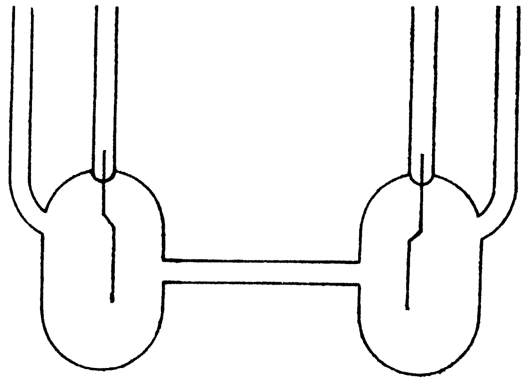

FIG. 1

area of the cross-section of the connecting tube is 0·07 sq. cm. The approximate resistance of normal KCl solution in this cell is 200 ohms. Since in the method employed the resistance of the diagonal arm containing the detecting instrument is practically ∞, (*i.e.* $G = \infty$), this cell can be used up to a strength as low as N/500 (*i.e.* up to a resistance of about 10^5 ohms) with the same degree of accuracy.

ARRANGEMENT OF APPARATUS

The arrangement of apparatus is shown in Fig. 2. It is the usual Wheatstone's bridge arrangement in which an amplifier is used in the galvanometer or telephone arm. The detecting instrument is the vertical wattmeter devised by Mukherjee (1930, 1938). This instrument is composed

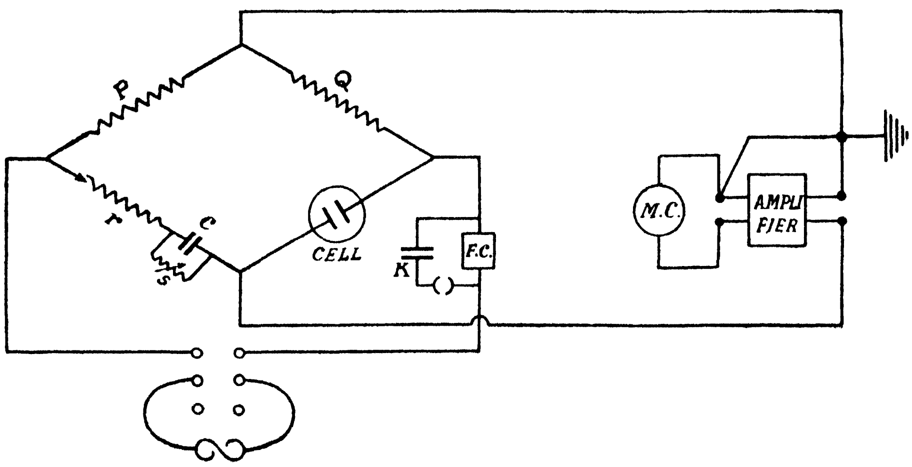

FIG. 2

of two systems of coils of which the fixed system produces the magnetic field and the moving system is deflected by the field. The former is put in the battery arm of the bridge and the latter in the out-put side of the amplifier. The ratio arms are of equal resistances so that their inductances are also the same. In the third arm, there is, in series with a resistance r, a condenser shunted by a variable resistance s. The effective resistance and reactance of the system composed of the condenser and the shunt are respectively $\frac{s}{1+s^2c^2p^2}$ and $-\frac{s^2cp}{1+s^2c^2p^2}$, where $p=2\pi$ times frequency. Therefore, when $V_c=V_D$, the resistance of the Ac-arm, namely,

$$r+\frac{s}{1+s^2c^2p^2}=R \quad \ldots \quad \ldots \quad \ldots$$

is equal to the resistance of the solution and the reactance, $-\frac{s^2cp}{1+s^2c^2p^2}$, balances the polarisation reactance of the solution as well as the residual inductive reactance of the Ac-arm.

METHOD OF FINDING THE BALANCE POINT

In detecting instruments of the wattmeter or dynamometer type, the deflection is given by

$$\delta=A I_f I_m \cos\psi$$

where I_f, I_m are the r.m.s. currents in the fixed coils and moving coils respectively and ψ, the phase-difference between them. The deflection is, therefore, zero when

$$(1)\ I_f \text{ or } I_m=0,$$

or

$$(2)\ \cos\psi=0 \quad i.e., \quad \psi=\frac{\pi}{2}.$$

The balance corresponding to condition (1) is called the true balance. In practice, the null point corresponding to condition (2) is easily obtained. If, however, the phase of the current through the fixed coil with respect to the current through the moving coil is altered by introducing a condenser, K, in parallel with the fixed coil, the null point is disturbed and there is deflection one way or the other according as I_f is in advance of, or behind, I_m

The procedure for finding true balance, is as follows:—

Keeping $s=0$, a null point is obtained by adjusting r, when the condenser K is off the circuit. Then the direction and extent of deflection are observed when K is introduced. The shunt is then given an arbitrary value and after obtaining the null-point by adjusting r with K off, the direction and extent of deflection are again observed with K on. Proceeding in this manner a condition is attained when null point will not be disturbed by introducing K. This condition corresponds to the true balance.

EARTHING

In working with alternating currents it is important to select the point which should be earthed. The question of earthing has been very elaborately the amplifier due to a defect in its make up, that current would only pass through the moving system and not through the fixed system. On the otherhand, to produce a deflection of the moving system, it is necessary that both the fixed and the moving systems must be traversed by currents from the same source.

Another feature was the use of very low voltage between the electrodes.

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